

Customized FORM PTO-1390		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY DOCKET NO. P06939US00/LRP
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/700494
INTERNATIONAL APPLICATION NO. PCT/JP99/02679	INTERNATIONAL FILING DATE 21 JANUARY 2000	PRIORITY DATE CLAIMED 03 JUNE 1998		
TITLE OF INVENTION: PROCESS FOR PRODUCING FLUOROALKYLCARBOXYLIC ACID				
APPLICANT(S) FOR DO/EO/US: ICHIHARA, Kazuyoshi et al.				
Applicant herewith submits to the US Designated/Elected Office (DO/EO/US) the following items and other information				
<input checked="" type="checkbox"/> 1. This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> 2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 USC 371. <input checked="" type="checkbox"/> 3. This express request to begin national examination procedures (35 USC 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 USC 371(b) and PCT Art. 22 and 39(1). <input checked="" type="checkbox"/> 4. A proper Demand for International Preliminary Examination was made by the 19 th month from the earliest claimed priority date. <input checked="" type="checkbox"/> 5. A copy of the International Application as filed (35 U.S.C. 371 (c)(2)) <input type="checkbox"/> a. is transmitted herewith (required only if not transmitted by the International Bureau). <input checked="" type="checkbox"/> b. has been transmitted by the International Bureau. <input type="checkbox"/> c. is not required, as the application was filed in the United States Receiving Office (RO/US). <input checked="" type="checkbox"/> 6. A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input checked="" type="checkbox"/> 7. Amendments to the claims of the International Appln. under PCT Article 19 (35 USC 371 (c)(3)) <input type="checkbox"/> a. are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> b. have been transmitted by the International Bureau. <input type="checkbox"/> c. have not been made; however, the time limit for making such amendments had NOT expired. <input checked="" type="checkbox"/> d. have not been made and will not be made. <input type="checkbox"/> 8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input checked="" type="checkbox"/> 9. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input checked="" type="checkbox"/> 10. A translation of the annexes to the Int'l Prelim. Exam. Report under PCT Article 36 (35 U.S.C. 371(c)(5)). Items 11. to 16. below concern document(s) or information included: <input type="checkbox"/> 11. An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98. <input checked="" type="checkbox"/> 12. An Assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> 13. A First preliminary amendment . <input type="checkbox"/> A Second or subsequent preliminary amendment. <input type="checkbox"/> 14. A substitute specification. <input checked="" type="checkbox"/> 15. A change of power of attorney and/or address letter. <input type="checkbox"/> 16. Other items or information: <input type="checkbox"/> <input type="checkbox"/> A copy of the Notification of Missing Requirements under 35 U.S.C. 371. <input type="checkbox"/> In the event that a petition for extension of time is required to be submitted herewith, and in the event that a separate petition does not accompany this response, applicant hereby petitions under 37 CFR 1.136(a) for an extension of time of as many months as are required to render this submission timely. Any fee is authorized in 17(c).				
Date: 16 NOVEMBER 2000				

U.S. APPLICATION NO. 09/700494		INTERNATIONAL APPLICATION NO. PCT/JP99/02679		ATTORNEY DOCKET NO P06939US00/LRP	
<input checked="" type="checkbox"/> 17. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
<input checked="" type="checkbox"/> Basic National Fee (37 CFR 1.492 (a) (1)-(5):					
<input type="checkbox"/> Neither Int'l Prelim. Exam. fee nor Int'l Search fee paid to USPTO		\$1000			
<input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO		\$ 860			
<input type="checkbox"/> No Int'l Prelim. Ex. fee paid to USPTO but Int'l Search fee paid to USPTO		\$ 710			
<input type="checkbox"/> International preliminary examination fee paid to USPTO		\$ 690			
<input type="checkbox"/> Int'l Prelim. Ex. fee paid to USPTO & all claims satisfied PCT Art. 33(1)-(4)		\$ 100			
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$860	
<input type="checkbox"/> Surcharge of \$130 for furnishing the oath or declaration later than from the earliest claimed priority date (37 CFR 1.492(e)).				<input type="checkbox"/> 20 mos. <input type="checkbox"/> 30 mos. + \$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	5 - 20 =		X \$18 =	\$	
Independent Claims	1 - 03 =		X \$80 =	\$	
<input type="checkbox"/> Multiple Dependent Claim(s) (if applicable)			+ \$270 =	\$	
TOTAL OF ABOVE CALCULATIONS =				\$ 860	
<input type="checkbox"/> Reduction of 1/2 for small entity status of applicant.				\$	
SUBTOTAL =				\$ 860	
<input type="checkbox"/> Processing fee of \$130 for furnishing the English translation later than from the earliest claimed priority date (37 CFR 1.492(f)).				<input type="checkbox"/> 20 mos. <input type="checkbox"/> 30 mos. + \$	
TOTAL NATIONAL FEE =				\$ 860	
<input checked="" type="checkbox"/> Fee for recording the enclosed assignment, accompanied by a cover sheet - \$40 per property				\$ 40	
TOTAL FEES ENCLOSED =				\$ 900	
Amount to be				Refunded	\$
				Charged	\$
<input checked="" type="checkbox"/> a. A check in the amount of \$900.00 to cover the above fees is enclosed.					
<input type="checkbox"/> b. Please charge my Deposit Account No. 12-0555 in the amount of \$ to cover the above fees.					
<input checked="" type="checkbox"/> c. The Commissioner is hereby authorized to charge any additional fees required or credit overpayment to Deposit Account No. 12-0555.					
Note: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
LINDA R. POTEATE			SIGNATURE: <u>Douglas E. Jackson</u>		
At the address (below) of CUSTOMER NO. 000881.			NAME: Douglas E. Jackson		
LARSON & TAYLOR, PLC			REG. NO.: 28518		
1199 NORTH FAIRFAX ST.			PHONE NO.: 703-739-4900		
SUITE 900			Date: 16 November 2000		
ALEXANDRIA, VA 22314					

09/700494
529 Rec'd PCT/PTC 16 NOV 2000
Patent

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of **ICHIHARA, et al.**)
New Application) Atty's Dckt:
Filed: On even date herewith) Application Branch
For: PROCESS FOR PRODUCING FLUOROALKYLCARBOXYLIC ACID

PRELIMINARY AMENDMENT

Hon. Assistant Commissioner of Patents
Washington, D.C. 20231

S I R:

Preliminary to the examination thereof, please amend the above-identified application as follows:

IN THE CLAIMS:

Claim 4, lines 1 and 2, delete "any one of claims 1-3", and insert therefor --claim 1--.

Claim 6, lines 1 and 2, delete "any one of claims 1-4", and insert therefor --claim 1--.

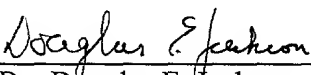
REMARKS

The above amendments are being made in order to place the application in better condition for examination and to reduce the filing fee.

Favorable consideration is respectfully requested.

Respectfully submitted,

Date: 11/16/00


By: Douglas E. Jackson
Registration No. 28518

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DESCRIPTION

PROCESS FOR PRODUCING FLUOROALKYLCARBOXYLIC ACID

TECHNICAL FIELD

This invention relates to a process for
5 producing a fluoroalkylcarboxylic acid that is a compound
industrially useful as a starting material for the
production of surfactants, pharmaceuticals, agricultural
chemicals.

BACKGROUND ART

10 Much research has been carried out on methods
for synthesizing carboxylic acid. Such methods are one of
the important reaction technologies in synthetic organic
chemistry. Known reactions for oxidizing alcohols,
aldehydes and the like include an oxygen oxidation
15 reaction using a solid catalyst; an oxidation reaction
using a chemical oxidizer such as chromic acid, potassium
permanganate, nitric acid or the like; and a liquid phase
autoxidation reaction. These conventional methods,
however, have problems such as high costs of solid
20 catalysts, difficulty in selective conversion to
carboxylic acid in some cases, and high toxicity of many
chemical oxidizers.

Methods are known for oxidizing a fluoroalkyl
alcohol to the corresponding fluoroalkylcarboxylic acid
25 with a comparatively high yield. Such methods include

methods using a chemical oxidizer, for example, potassium dichromate/sulfuric acid (T. Hudlicky et al., J. Fluorine Chem., (1992), 59(1), 9-14), potassium permanganate (I. Lehms et al., DD 268685), or nitrogen dioxide (R. M. Scribner, J. Org. Chem., (1964), vol.29, 279-283 or ibid., (1964), vol.29, 284-286); and methods using an organic or inorganic acid copper salt catalyst/alkali/oxygen (I. P. Skibida et al., WO 93/12059). These methods, however, have the following problems. The method using chromic acid or potassium permanganate has waste disposal problems after reaction. According to the method using nitrogen dioxide, the reaction takes 10 hours or more using 2 equivalents of nitrogen dioxide. Moreover, use of an increased amount of nitrogen dioxide and/or a higher reaction temperature will increase byproducts. The oxidation method using an organic or inorganic acid copper salt catalyst/alkali/oxygen only achieves a low selectivity to carboxylic acid and also has separation and purification problems such as difficulty in removal of the catalyst and the solvent after reaction.

Methods for oxidizing a fluoroalkyl alcohol to the corresponding fluoroalkylcarboxylic acid using nitric acid are described, for example, in D. R. Bear, Ind. Eng. Chem., (1959), vol.51, 829-830 and in Y. Desirant, Bull. Sci. acad. roy. Belg., (1929), vol.15, 966-982. However,

Desirant reports that the method has the following problems: the reaction requires using about 2.5 equivalents of nitric acid relative to the alcohol and it takes 2.5 days under reflux to complete the reaction. In hydrocarbon oxidation using nitric acid, it is known that oxygen is introduced into the reaction system to reduce the required amount of nitric acid to a stoichiometric amount or less relative to the reaction substrate (John W. Ager, Jr. DE 2116212). Such technique, however, is not known in fluoroalkyl alcohol oxidation using nitric acid.

DISCLOSURE OF INVENTION

A principal object of this invention is to obviate the defects of the conventional production methods and provide a process for producing a fluoroalkylcarboxylic acid with high selectivity at low costs.

The present inventors carried out extensive research in view of the above prior art problems and found that fluoroalkylcarboxylic acids can be produced with high conversion and high selectivity by oxidizing fluoroalkyl alcohols using nitric acid as an oxidizing agent.

The present invention provides the following processes for preparing fluoroalkylcarboxylic acids.

1. A process for producing a fluoroalkylcarboxylic acid of the formula $R_f\text{COOH}$ wherein R_f is a C_{1-16} fluoroalkyl

group, which comprises oxidizing a fluoroalkyl alcohol of the formula $RfCH_2OH$ wherein Rf is as defined above using nitric acid.

2. The process according to item 1 wherein the oxidation
5 is carried out in the presence of a metal catalyst.

3. The process according to item 2 wherein the metal catalyst is at least one metal selected from the group consisting of iron, nickel, copper and vanadium, or at least one oxide or salt of these metals.

10 4. The process according to any one of items 1-3 wherein a fluoroalkylcarboxylic acid of the formula $RfCOOH$ wherein Rf is as defined above has been placed and is present in the reaction system at the beginning of the reaction.

5. The process according to any one of items 1-4 wherein
15 oxygen is fed into the reaction system during the reaction.

6. The process according to item 5 wherein oxygen is fed into the reaction system to reduce the required amount of nitric acid to a stoichiometric amount or less relative to the fluoroalkyl alcohol of the formula $RfCH_2OH$ wherein Rf
20 is as defined above.

The method of the present invention comprises converting a fluoroalkyl alcohol into the corresponding fluoroalkylcarboxylic acid by oxidation using nitric acid.

The fluoroalkyl alcohol used in the present
25 invention is represented by the formula $RfCH_2OH$ wherein Rf

is a C_{1-16} fluoroalkyl group. Specific examples include fluoroalkyl alcohols represented by $H(CF_2)_nCH_2OH$ or $F(CF_2)_nCH_2OH$ wherein n is an integer of 1 to 16. Of the alcohols represented by $H(CF_2)_nCH_2OH$, preferable are those
5 wherein n is an integer of 2, 4, 6, 8, 10, 12, 14 or 16. Of the alcohols represented by $F(CF_2)_nCH_2OH$, preferable are those wherein n is an integer of 1 to 3.

The nitric acid used in the present invention has a concentration of 5% or higher, preferably 30% to 70%.

10 The molar ratio of nitric acid to the starting fluoroalkyl alcohol is 2 or less, i.e., a stoichiometric amount or less, and is usually in the range of 0.1 to 2, preferably 0.3 to 1.

The molar ratio of nitric acid to the starting
15 alcohol may vary depending on the starting alcohol. As the fluoroalkyl group of the starting fluoroalkyl alcohol has a longer chain, a larger molar ratio of nitric acid to the fluoroalkyl alcohol is preferred.

The metal catalyst to be used in the present
20 invention is preferably at least one metal such as iron, nickel, copper, vanadium and the like, or at least one oxide or salt of these metals, of which copper powder, iron chloride (II), iron chloride (III), nickel chloride, copper chloride, ammonium vanadate and vanadium oxide (V)
25 are particularly preferred.

The weight ratio of the metal catalyst to the starting alcohol is usually at least 0.000001, preferably in the range of 0.00001 to 0.1. The use of an increased amount of the metal catalyst can reduce the reaction
5 pressure and reaction temperature. An excess of the metal catalyst, however, will convert the reaction product fluoroalkylcarboxylic acid to a metal salt, thus adversely affecting the separation and purification operation.

The reaction is usually carried out at
10 temperatures in the range of 80°C to 200°C, preferably 100°C to 150°C.

By the end of the reaction, the reaction pressure may increase to a maximum of 2.5 MPa (gauge pressure). In consideration of the price of the reactor
15 and other factors, it is preferable that the reaction be carried out while controlling the reaction pressure. A preferable method for controlling the reaction pressure comprises supplying oxygen so as to control the reaction pressure to 0.4 to 1.0 MPa (gauge pressure) during the
20 reaction.

Feeding oxygen into the reaction system not only reduces the molar ratio of nitric acid to a fluoroalkyl alcohol but also helps to control the reaction pressure. Furthermore, it is unnecessary to eliminate nitrogen
25 oxides during the reaction. A preferred method for

feeding oxygen into the reaction system comprises supplying oxygen at any time when necessary during the reaction.

Oxygen is continuously fed into the reaction system until the conversion of the starting fluoroalkyl alcohol reaches 100%. The required amount of oxygen is 0.7 to 0.9 mole per mole of the starting fluoroalkyl alcohol.

In pressure control using oxygen, it is preferable that as the fluoroalkyl group of the starting fluoroalkyl alcohol has a longer chain, the reaction pressure should be set to a higher value.

When a fluoroalkylcarboxylic acid is placed into the reaction system before reaction so that carboxylic acid is present at the beginning of the reaction, the reaction pressure may be set to a lower value. The amount of the fluoroalkylcarboxylic acid is preferably 0.01 to 2 moles, more preferably 0.1 to 1 mole, per mole of the starting fluoroalkyl alcohol.

The reaction time is usually within the range of about 10 to about 20 hours. As the reaction pressure is set to a higher value, a shorter reaction time will result. When a fluoroalkylcarboxylic acid and/or a metal salt catalyst is present, the reaction time can be reduced to 4 to 8 hours.

Upon completion of the reaction, nitrogen oxides can be removed by a known removal method such as a dry method, a wet method or the like.

When the obtained fluoroalkylcarboxylic acid of the formula $RfCOOH$ is a fluoroalkylcarboxylic acid wherein Rf is a fluoroalkyl group having at least 4 carbon atoms, the reaction mixture separates into two layers of liquids upon completion of the reaction. The upper layer is a nitric acid layer. The fluoroalkylcarboxylic acid in a concentrated form is present in the lower layer.

Fluoroalkylcarboxylic acid, which is the desired compound of the present invention, can be isolated and purified by known methods. Examples of useful procedures are extraction, distillation, recrystallization, column chromatography and the like.

The method according to the present invention obviates the defects of the conventional production methods and produces a fluoroalkylcarboxylic acid with high selectivity at low costs.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described below in more detail with reference to Examples.

Example 1 (a case in which the reaction pressure was controlled using oxygen)

$H(CF_2)_6CH_2OH$ (664.00 g, 2.00 moles), 55% nitric

acid (114.55 g, 1.00 mole) and $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$ (0.0066 g) were placed into an autoclave equipped with a 1000-ml glass pressure vessel, a fluoroplastic upper cover, stirring blades, a thermometer protection tube, a fluoroplastic insert tube, a pressure gauge, a safety valve and a supply line from an oxygen bomb. The mixture was stirred with heating, upon which reaction pressure began to increase. 3.1 hours after the start of heating, the reaction temperature rose to 125°C and the reaction pressure increased to 0.6 MPa (gauge pressure; the same hereinafter). From that time, oxygen was fed into the gas phase at various times in an amount of 0.35 g (11.00 mmoles) per time, whereby the reaction pressure was controlled to 0.6 MPa. 6.5 hours after the start of heating, complete consumption of the starting fluoroalkyl alcohol was confirmed by gas chromatography to confirm the completion of the reaction [$\text{H}(\text{CF}_2)_6\text{CH}_2\text{OH}$ conversion: 100.0 g.c.% (gas chromatography %; the same hereinafter); $\text{H}(\text{CF}_2)_6\text{COOH}$ selectivity: 100.0 g.c.%]. In total, 46.72 g (1.46 moles) of oxygen was fed into the gas phase by the end of the reaction. After completion of the reaction, oxygen was continuously supplied so as to convert residual nitrogen oxides into nitric acid. Then the residual pressure was released. Because of the reaction mixture being provided in the form of two layers of liquids,

765.78 g of a crude carboxylic acid $[\text{H}(\text{CF}_2)_6\text{COOH}]$ was obtained in a concentrated form from the lower layer by means of liquid-liquid separation at the cease of stirring.

The crude carboxylic acid was purified by distillation

- 5 under reduced pressure, giving 499.75 g of a carboxylic acid $[\text{H}(\text{CF}_2)_6\text{COOH}]$ in high purity (99 g.c.% or higher) with an isolation yield of 65.26 mole %.

Example 2 (a case in which a fluoroalkyl group having a long chain was used)

- 10 $\text{H}(\text{CF}_2)_8\text{CH}_2\text{OH}$ (500.00 g, 1.16 moles), 55% nitric acid (132.87 g, 1.16 moles) and $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$ (0.0050 g) were placed into the autoclave used in Example 1. The mixture was heated with stirring in the same manner as in Example 1. 3.8 hours after the start of heating, the reaction
- 15 temperature rose to 125°C and the reaction pressure increased to 0.8 MPa. From that time, oxygen was fed into the gas phase in the same manner as in Example 1, whereby the reaction pressure was controlled at 0.8 MPa. 7.0
- hours after the start of heating, complete consumption of
- 20 the starting fluoroalkyl alcohol was confirmed by gas chromatography to confirm the completion of the reaction $[\text{H}(\text{CF}_2)_8\text{CH}_2\text{OH}]$ conversion: 100.0 g.c.%; $[\text{H}(\text{CF}_2)_8\text{COOH}]$ selectivity: 99.6 g.c.%]. The same procedure as in
- Example 1 was followed and 651.93 g of a crude carboxylic
- 25 acid $[\text{H}(\text{CF}_2)_8\text{COOH}]$ was obtained in a concentrated form

from the lower layer by means of liquid-liquid separation. The crude carboxylic acid was purified by distillation under reduced pressure, giving 475.13 g of a carboxylic acid $[H(CF_2)_8COOH]$ in high purity (96 g.c.% or higher)

5 with an isolation yield of 72.88 mole %.

Example 3 (a case in which a fluoroalkylcarboxylic acid was added before reaction)

$H(CF_2)_8CH_2OH$ (518.40 g, 1.20 moles), $H(CF_2)_8COOH$ (269.60 g, 0.60 mole), 55% nitric acid (137.45 g, 1.20
10 moles) and $FeCl_2 \cdot nH_2O$ (0.0079 g) were placed into the autoclave used in Example 1. The mixture was heated with stirring in the same manner as in Example 1. 2.6 hours after the start of heating, the reaction temperature rose to 125°C and the reaction pressure increased to 0.6 MPa.
15 From that time, oxygen was fed into the gas phase in the same manner as in Example 1, whereby the reaction pressure was controlled at 0.6 MPa. 5.4 hours after the start of heating, complete consumption of the starting fluoroalkyl alcohol was confirmed by gas chromatography to confirm the
20 completion of the reaction [$H(CF_2)_8CH_2OH$ conversion: 100.0 g.c.%; $H(CF_2)_8COOH$ selectivity: 99.6 g.c.%]. The same procedure as in Example 1 was followed and 835.36 g of a crude carboxylic acid $[H(CF_2)_8COOH]$ was obtained in a concentrated form from the lower layer by means of liquid-
25 liquid separation. The crude carboxylic acid was purified

by distillation under reduced pressure, providing 586.04 g of a carboxylic acid [$\text{H}(\text{CF}_2)_8\text{COOH}$] in high purity (96 g.c.% or higher) with an isolation yield of 72.19 mole %. By subtracting the amount of $\text{H}(\text{CF}_2)_8\text{COOH}$ originally fed, the amount of $\text{H}(\text{CF}_2)_8\text{COOH}$ produced in Example 3 was found 392.85 g.

Example 4 (a case of not separating into a nitric acid layer and another liquid layer)

$\text{CF}_3\text{CH}_2\text{OH}$ (200.00 g, 2.00 moles), 55% nitric acid (114.55 g, 1.00 mole) and $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$ (0.0020 g) were placed into the autoclave used in Example 1. The mixture was heated with stirring in the same manner as in Example 1. 3.0 hours after the start of heating, the reaction temperature rose to 125°C and the reaction pressure increased to 0.75 MPa. From that time, oxygen was fed into the gas phase in the same manner as in Example 1, whereby the reaction pressure was controlled at 0.75 MPa. 6.0 hours after the start of heating, complete consumption of the starting fluoroalkyl alcohol was confirmed by gas chromatography to confirm the completion of the reaction [$\text{CF}_3\text{CH}_2\text{OH}$ conversion: 100.0 g.c.%; CF_3COOH selectivity: 98.5 g.c.% or higher]. The same procedure as in Example 1 was followed, thus giving an aqueous nitric acid solution of CF_3COOH (361.18 g, a material balance of 99.43 mass %).

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CLAIMS

1. (Amended) A process for producing a fluoroalkylcarboxylic acid of the formula $RfCOOH$ wherein Rf is a C_{1-16} fluoroalkyl group, which comprises oxidizing a fluoroalkyl alcohol of the formula $RfCH_2OH$ wherein Rf is as defined above using nitric acid and feeding oxygen into the reaction system during the oxidation reaction.

2. The process according to claim 1 wherein the oxidation is carried out in the presence of a metal catalyst.

3. The process according to claim 2 wherein the metal catalyst is at least one metal selected from the group consisting of iron, nickel, copper and vanadium, or at least one oxide or salt of these metals.

4. The process according to any one of claims 1-3 wherein a fluoroalkylcarboxylic acid of the formula $RfCOOH$ wherein Rf is as defined above is present in the reaction system at the beginning of the reaction.

5. (Cancelled)

6. (Amended) The process according to any one of claims 1-4 wherein oxygen is fed into the reaction system to reduce the required amount of nitric acid to a stoichiometric amount or less relative to the fluoroalkyl alcohol of the formula $RfCH_2OH$ wherein Rf is as defined above.

ABSTRACT

The present invention provides a process for producing a fluoroalkylcarboxylic acid of the formula
5 R_fCOOH wherein R_f is a C_{1-16} fluoroalkyl group, which comprises oxidizing a fluoroalkyl alcohol of the formula R_fCH_2OH wherein R_f is as defined above using nitric acid.

The process according to the present invention produces a fluoroalkylcarboxylic acid with high
10 selectivity at low costs.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent

In re patent application of: ICHIHARA et al.

Serial No.: New Application

Examiner:

Filed: On even date herewith

Art Unit:

For: PROCESS FOR PRODUCING

Atty. Dckt No.: P06939US00

FLUOROALKYLCARBOXYLIC ACID

CHANGE OF CORRESPONDENCE ADDRESS
CUSTOMER NUMBER DESIGNATION

Honorable Assistant Commissioner for Patents
Washington, D.C.

S I R:

Henceforth, please **change the correspondence address** of the above identified application to the correspondence address associated with the CUSTOMER NUMBER identified below, or to the (same) correspondence address shown below if the Customer Number designation cannot be used.

LARSON & TAYLOR, PLC
Transpotomac Plaza
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Alexandria, VA 22314

or


CUSTOMER NUMBER
00881

In addition, please also **appoint the practitioners** (of LARSON & TAYLOR, PLC) associated with this Customer Number to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

If there is any problem in changing the correspondence, please contact the undersigned immediately by telephone at 703-739-4900.

Respectfully submitted,

Date: 11/16/00



By: Douglas E. Jackson

Registration No.: 28518

LARSON & TAYLOR, PLC • 1199 North Fairfax St. • Suite 900 • Alexandria, VA 22314

DECLARATION FOR USA PATENT APPLICATION

(including Design and National Stage PCT)

Attorney's Docket ID: _____

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below adjacent to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled PROCESS FOR PRODUCING FLUOROALKYL CARBOXYLIC ACID

_____, the specification of which

_____ is attached hereto. (or)

☒ was filed on May 20, 1999, ☐ and was amended on January 21, 2000

☐ as U.S. Application No. _____ (or)

☒ as International PCT Application No. PCT/JP99/02679

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a) - (d) or §365 (b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, where priority is not claimed, any foreign application for patent or inventor's certificate, or any PCT International application, having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) (____ ADDITIONAL APPLICATIONS IDENTIFIED ON ATTACHED SHEET):

Number	Country	Day/Month/Year Filed	Priority Not Claimed
<u>1998-154507</u>	<u>Japan</u>	<u>03/06/1998</u>	<u>_____</u>

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or §365(c) of any PCT International application designating the U.S., listed below; and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application. (____ ADDITIONAL APPLICATIONS IDENTIFIED ON ATTACHED SHEET.)

Application Serial No.	Day/Month/Year Filed	Status - patented, pending, abandoned
_____	_____	_____

I hereby appoint the practitioners of LARSON AND TAYLOR associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and direct that all correspondence be addressed to that Customer Number.

CUSTOMER NUMBER: 00881

Direct all telephone calls to _____, at TEL (703) 920-7200 (Fax: 703-892-8428)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00
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SEE ATTACHED SHEET FOR SIMILAR INFORMATION AND SIGNATURE FOR ADDITIONAL JOINT INVENTORS.
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